

Operation of Platinum—Palladium Catalysts with Leaded Gasoline

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The effect of various fuel additives on the ability of platinum-palladium catalytic converters to remove the carbon monoxide and hydrocarbon components of automotive exhaust has been examined. Engine dynamometer studies suggest that these catalysts may be successfully used in conjunction with fuels of relatively high tetraethyllead concentrations, provided the ethylene dibromide portion of the scavenger is excluded.

It has been amply demonstrated that the use of leaded fuel rapidly inactivates a noble metal oxidation catalyst used to control hydrocarbon and CO emissions in a motor vehicle (1-7). This limits their use to unleaded fuel. For this reason, the Federal government has mandated the availability in the U.S. of unleaded fuel, containing no more than 0.05 g/gal of lead (8). This limitation applies to both base metal, as well as precious metal oxidation catalysts, containing platinum and palladium, of the type expected to be generally used in 1975 model vehicles.

In view of the advantages of using leaded fuel in all vehicles, we have some interesting and significant results to report regarding the possibility of operating catalytic vehicles on leaded fuel. This information is of a preliminary nature, based on laboratory and dynamometer tests. No "on the road" vehicle studies have, as yet, been made. Because of the social and economic issues involved, the Chrysler Corporation is making this new knowledge on the subject immediately avail-

able to the various industries and to the government for further study.

The effect of using a noble metal catalytic converter with an engine running on fuel containing various additives was examined via engine dynamometer tests. The dynamometer test, to stabilize catalyst performance, consists of an initial 10 hr running on fuel containing no added lead antiknock. This is followed by 10 hr of operation on the same fuel containing the additive in question. A final 10 hr of operation, again on unleaded fuel, measures the extent of permanent deterioration.

Figure 1 shows that when standard leaded gasoline is used as the modified fuel, there is an abrupt loss in catalytic CO removal from 95% to 30%. A subsequent 10 hr of operation again on unleaded fuel shows a fairly rapid, but not complete, recovery of catalytic activity back to 88% removal.

In view of the rapid recovery of the catalyst, it appeared unlikely that the deposition of solid lead compounds, which occurs during operation of catalysts on leaded fuel (5,6,9), is the cause of the large activity loss. Thus, another mechanism was sought.

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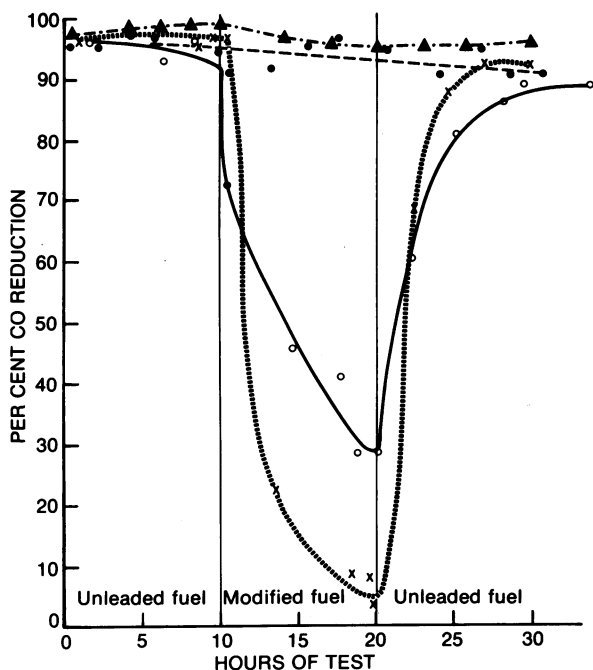


FIGURE 1. Multicylinder engine dynamometer studies of the effects of various modified fuels on the ability of noble metal catalysts to remove carbon monoxide emissions. The modified fuels contain: (—○) 3 g Pb/gal with motor mix scavengers; (---●) 3 g Pb/gal without scavengers; (---x) no lead, but containing ethylene dichloride and ethylene dibromide in the amount normally used with 3 g Pb/gal; (—▲) 2 g Pb/gal with 1.0 theory ethylene dichloride.

Scavengers are normally added with the tetraethyllead during the production of commercial leaded fuel. This scavenger typically consists of sufficient ethylene dichloride to form lead chloride with the lead present (1.0 theory), plus half as much additional ethylene dibromide (0.5 theory). This combination of tetraethyllead and scavengers is termed "motor mix". These organic halides are soluble in the gasoline and form volatile lead halides during engine combustion. These volatile halides carry the lead out of the combustion chamber, to minimize the accumulation of lead on spark plugs, exhaust valves, and combustion chamber walls.

When fuel containing no lead, but only the mixed scavenger is burned, the catalyst shows an even more severe inactivation (Fig. 1). Again, the recovery of catalyst activity on pure gasoline, (no lead, no

scavenger) compared with use of a fuel containing only scavengers, is prompt and nearly complete.

When leaded fuel is used, but with no scavenger, there is only a small loss in activity (Fig. 1). Similarly, a leaded fuel containing only the ethylene dichloride portion of the scavenger again exhibits little loss in activity. A small permanent loss is encountered with both fuels.

Through a series of studies on synthetic gases, and on single cylinder and multicylinder engine dynamometer measurements, we have identified the ethylene dibromide part of the scavenger as the component which inactivates platinum-palladium oxidation catalysts. The use of either ethylene dichloride alone or no scavenger in leaded fuel results in only a small catalyst inactivation. This effect is similar for both carbon monoxide and hydrocarbon oxidation by the catalyst.

Figure 2 presents more extended dyna-

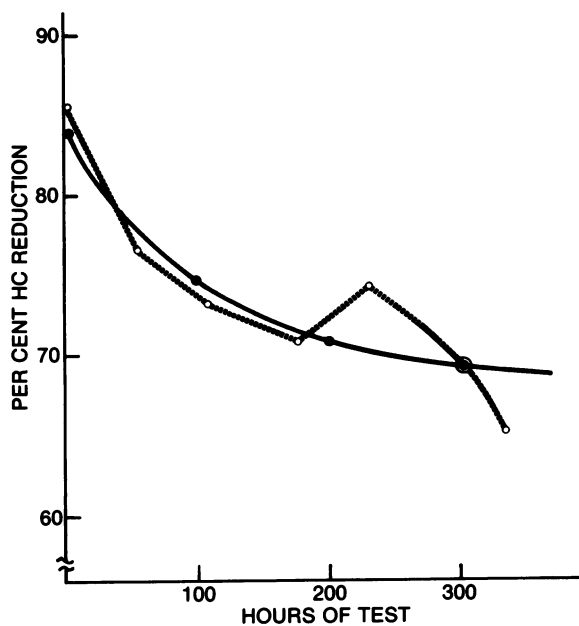


FIGURE 2. Multicylinder engine endurance tests, comparing platinum-palladium catalyst deterioration on (—○) 1975-type "unleaded" fuel containing 0.05 g Pb/gal as motor mix, vs. (---●) modified fuel containing 1.5 g Pb/gal without scavengers. Catalytic hydrocarbon removal is measured.

momometer endurance results. The solid line shows the catalytic activity for hydrocarbon oxidation when a 1975-type "unleaded" fuel, containing 0.05 g lead/gal is used. This shows a slow deterioration in catalyst activity which is typical of prototype 1975 automotive units. It is the average for five catalyst samples; best expressed by the exponential equation: (standard deviation $\sigma = 2.97$).

$$Y = 67.86 + 15.16 e^{-x/100} \quad (1)$$

A test run of 300 hr (cyclic test, alternating between idle and moderately heavy engine load) is equivalent to about 25,000 miles of vehicle operation.

The dotted line shows the catalyst activity loss, using a fuel containing 1.5 g lead/gal, with no scavenger. The small loss in activity is comparable to that with "unleaded" fuel. The equation for lead-no-scavenger fuel is given in eq. (2).

$$Y = 67.80 + 16.92 e^{-x/100} \quad (2)$$

with $\sigma = 2.40$. The data indicate that the two fuels produce equivalent catalyst performance, and that the individual points with lead-no-scavenger fuel show comparable variance.

As yet, we have run no extended mileage car tests with a leaded fuel containing no scavenger.

The use of commercially leaded fuels is attractive for several reasons. The elimination of lead has several adverse supply effects (10,11): (a) less efficient conversion of petroleum to gasoline with an adequate octane rating; (b) a progressive increase, with extended mileage, in octane need for cars running on unleaded fuel; (c) loss of the broad availability of fuel for 1975 vehicles because of the restricted availability of unleaded fuel. The continued use of leaded fuel would improve the gasoline supply and simplify the problem of the automobile owner in finding fuel for his 1975 catalyst-equipped car.

There is some concern that the wide use of catalysts to minimize vehicle emissions will increase the formation and discharge of

SO₃ (sulfate) to the atmosphere. Evidence has been cited that a catalyst increases the sulfate emission (12,13).

We find that both catalytic and noncatalytic vehicles emit some SO₃ when running on unleaded fuel. Leaded fuel, however, reduces the emissions of SO₃ on noncatalyst cars. For example, vehicles equipped with either catalyst or noncatalyst systems emit as SO₃ an average of 14.7% of the sulfur present in the fuel when running extended mileages on unleaded fuel. However, similar noncatalyst vehicles running on leaded fuel emit, on the average, only 6% of the sulfur as SO₃.

The analysis of exhaust deposits from both noncatalyst and catalyst vehicles suggests that a portion of the lead forms inert lead sulfate with exhaust SO₃. The lead sulfate is principally retained in the exhaust system, as are most lead compounds. This result suggests that the broad present use of leaded fuel is actually minimizing sulfate emission from present vehicles.

Those conversant with the function of the scavenger in leaded fuel (14,15) suggest that its elimination would produce some problems of spark plug fouling and engine exhaust valve durability. The ethylene dibromide part of the scavenger mix is actually the most effective for preventing these problems. However, the use of ethylene dichloride only would involve appropriate and more costly metallurgical changes. These modifications may make it possible to use a single, leaded fuel for both catalyst and noncatalyst vehicles. Much further engineering and vehicle testing is necessary.

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